II. Environmental Requirements

PROJECT ENGINEERING DIVISION

A. Multi-Phase Ammonia–Water System (Rev. 1)[1], C. *Haudenschild*

1. Introduction

In conjunction with the SR/AD Space Vehicle Design Criteria Monograph Program JPL develops monographs on various planetary environments. In the specific problem of modeling atmospheres of Jupiter and Saturn for the monographs one needs to consider the properties of the major condensible constituents—ammonia and water.

Pertinent information in references is primarily in a scattered tabular form.

In Ref. 1 Lewis makes a graphical representation of the NH_3–H_2O system from data in Refs. 2 and 3. For the production of model atmospheres it was felt that analytic expressions, in addition to a graphical display, would be very useful. So, an attempt was made to produce empirical equations relating quantities of interest displayed in Table 1. The equations give partial vapor pressure over solid NH_3, solid $(NH_3)_2H_2O$ hydrate, solid NH_3H_2O hydrate, solid H_2O, and NH_3–H_2O solution phases. In addition, along boundaries of the regions, equations for freezing curve temperatures as a function of concentration are given. Finally a phase diagram similar to Lewis's is produced, displaying the equations graphically.

Table 1. Definition of terms

Symbol	Units	Definition
T	°K	Temperature
C	$0.0 \leq C \leq 1.0$	Molar concentration of NH_3 in H_2O solution
P_2	Torr	H_2O vapor partial pressure
P_3	Torr	NH_3 vapor partial pressure

2. Forms Relating the Quantities of Interest

To proceed, we must choose appropriate equation forms that can be fitted to the data available and incorporate our understanding of the physics of the situation. The following forms were chosen:

[1]This article is a revision of "Multi-Phase Ammonia–Water System," C. Haudenschild, in SPS 37-64, Vol. III, pp. 4–9, and contains revised tabular data.

In the pure solid regions of NH_3 or H_2O, equations of the form of the Clausius Clapeyron equation are chosen to relate P and T (Ref. 1):

$$\log P = \alpha - \beta/T \tag{1}$$

The constants α and β can be determined numerically from any two data points at which P and T are specified.

Forms for the hydrate regions were taken from Ref. 1. For $(NH_3)_2H_2O$ we get the equation

$$(2/3)\log P_3 + (1/3)\log P_2 = \alpha - \beta/T \tag{2}$$

Here the ratio of the coefficients of the logarithms of the pressures is the same as the ratio of NH_3 and H_2O in the hydrate—that is, two to one—and the basic form of the Clausius Clapeyron equation is retained. For NH_3H_2O the appropriate equation is

$$(1/2)\log P_2 + (1/2)\log P_3 = \alpha - \beta/T \tag{3}$$

In each hydrate region one can obtain the two constants α and β numerically from two data points, just as for the pure solid regions.

From the phase diagram displayed in Ref. 1 (p. 367) we infer that solution region equations obey:

$$\left(\frac{\partial \log P_3}{\partial \log P_2}\right)_C = \text{constant, independent of temperature} \tag{4}$$

That is, the isoconcentration lines are straight. Also, we infer that

$$\left(\frac{\partial \log P_3}{\partial \log P_2}\right)_T = -\frac{1-C}{C}, \text{ also independent of temperature.} \tag{5}$$

This matches the slope of the solution region isotherm with the slopes in the hydrate regions, at those points where the molecular number ratios are identical in the two regions. Equations were chosen which retain a Clausius Clapeyron dependence and satisfy the above requirements; namely

$$\log P_2 = \log(1-C) + A_0 + A_2C^2 - \frac{a_0 + a_2C^2}{T} \tag{6}$$

and

$$\log P_3 = \log C + B_0 + A_2(C^2 - 2C) - \frac{b_0 + a_2(C^2 - 2C)}{T} \tag{7}$$

The six constants A_0, A_2, B_0, a_0, a_2, and b_0 can be obtained numerically from appropriately chosen combinations of tabular values of C, T, $\log P_2$, and $\log P_3$.

Finally, freezing curves can be obtained by equating the solution region partial pressures to solid region ones, and eliminating the pressures. There result equations which give T as a function of C.

3. Numerical Relations Among Quantities of Interest

Table 2 lists numerical equations for regions of solid and solution phases. Partial pressures of ammonia and water are given as function of temperature or of temperature

Table 2. Solid and solution equations

Region	Data source	Form	Equation
Solid H_2O	Table 3 (underlined entries)	Eq. (1)	$\log P_2 = 10.447 - 2673.01/T$ (8)
Solid NH_3	Table 4 (underlined entries)	Eq. (1)	$\log P_3 = 10.312 - 1691.77/T$ (9)
$(NH_3)_2H_2O$	Table 5 († entries)	Eq. (2)	$(2/3)\log P_3 + (1/3)\log P_2 = 9.777 - \frac{2051.185}{T}$ (10)
NH_3H_2O	Table 5 (‡ entries)	Eq. (3)	$(1/2)\log P_2 + (1/2)\log P_3 = 9.790 - \frac{2219.28}{T}$ (11)
Solution	Table 5 (underlined entries)	Eq. (6)	$\log P_2 = \log(1-C) + 9.488 + 1.743C^2 - \left(\frac{2406.2 + 878.192C^2}{T}\right)$ (12)
		Eq. (7)	$\log P_3 = \log C + 9.906 + 1.743(C^2 - 2C) - \left(\frac{2149.65 + 878.192(C^2 - 2C)}{T}\right)$ (13)

and concentration. The data from which the numerical coefficients in Table 2 were derived are found in Tables 3, 4, and 5.

Table 6 lists numerical freezing curves temperature equations as functions of concentration. These are formed by equating the source equation and eliminating log P_2, log P_3, or both.

4. Comparison With Data

Table 3 compares the values of log P_2 for solid H_2O from the tabular sources listed with log P_2 from Eq. (8). The largest discrepancy shown is near −99°C and amounts to 0.02 in log P_2.

Table 3. Vapor pressure over solid H_2O ice

Reference and page	T, °C	T, °K	P_2, torr (From Ref.)	log P_2, torr (From Ref.)	log P_2, torr (From Eq. 8)
4, 1474	−99.0	174.16	1.2×10^{-5}	−4.92	−4.901
4, 1474	−68.0	204.46	2.36×10^{-3}	−2.627	−2.627
4, 1474	−46.0	227.16	0.0481	−1.318	−1.320
4, 1474	−20.1	253.06	0.0769	−1.114	−1.116
4, 1475	0.0	273.16	4.579	0.661	0.661

Underlined entries indicate data used to obtain constants in Eq. (8).

Table 4. Vapor pressure over solid NH_3 ice

Reference and page	T, °C	T, °K	P_3, torr (From Ref.)	log P_3, torr (From Ref.)	log P_3, torr (From Eq. 9)
2, 362	−77.6	195.56	45.82	1.661	1.661
3, D-140	−79.2	193.96	40.0	1.602	1.590
2, 362	−84.4	188.76	22.36	1.348	1.349
4, D-140	−91.9	181.26	10.0	1.000	0.979
3, D-140	−109.1	164.06	1.00	0.000	0.000

Underlined entries are data used to obtain constants in Eq. (9).

Table 4 compares values of log P_3 for solid NH_3 from the tabular sources listed with log P_3 from Eq. (9). The largest discrepancy shown is near −91.9°C and amounts also to 0.02 in log P_3.

Table 5 was produced to display the accuracy of the solution and freezing curve equations. Column 1 gives the concentration considered on any particular line. Column 2 lists the tabular source from which T (°K), log P_2, and log P_3 in Cols. 3, 4, and 5 were obtained. When an S in the "remarks" column appears, we are considering the solution region and the temperature in Col. 3 is transferred to Col. 7. F denotes freezing curve; hence, T in Col. 7 is computed from the appropriate freezing curve equation. Finally, based on the values of C in Col. 1 and T in Col. 7, log P_2 and log P_3 in Cols. 8 and 9 are obtained from Eqs. (12) and (13).

The largest discrepancy in log P_3 (Cols. 5 and 9 in Table 5) in the solution region occurs at $C = 0.60$ and $T = 189.31$ and is 0.15 (a factor of 1.4). Table values for log P_2 are only given in the interval $0 \leq C \leq 0.2395$. The largest discrepancy in log P_2 (Cols. 4 and 8 in Table 5) in the solution region occurs at $C = 0.2181$ and $T = 316.16$ and is 0.14 (a factor of 1.4).

For points along the freezing curves, discrepancies of log P_2 and log P_3 are magnified. That is, the freezing curve temperature is used to calculate the log pressure instead of the table temperature, as in the solution region. Hence, a double error is produced. The largest discrepancy in log P_3, listed in Table 5, occurs at $C = 0.25$ and is 0.387 (a factor of 2.4). Values of log P_2 are listed in the tables at only five points along the freezing curve, all of which have $0 \leq C \leq 0.2$. Among these the largest discrepancy occurs at $C = 0.20$ with log P_2 0.33 below the tabular value (a factor of 2.1). One would expect relatively large discrepancies along the freezing curve in the region of $0.2 \leq C \leq 0.35$, because T is a very sensitive function of C there (Fig. 1). In fact, if one scans the freezing curve temperature, the largest discrepancy of 9.8°K occurs at

Table 5. Vapor pressure over NH_3–H_2O solution

C	Reference and page	T, °K (from Ref.)	log P_2, torr (from Ref.)	log P_3, torr (From Ref.)	Remarks	T, °K (See Subsection 4.)	log P_2, torr (Eq. 12)	log P_3, torr (Eq. 13)
1.00	2, 362	—	—	—	S	273.16	−∞	3.508
1.00	↓	195.56	—	1.661	F	195.59	−∞	1.662
0.95		192.66	—	1.537	F	192.95	−6.818	1.544
0.95		213.16	—	2.194	S	213.16	−5.246	2.170

Table 5 (contd)

C	Reference and page	T, °K (from Ref.)	log P_2, torr (from Ref.)	log P_3, torr (From Ref.)	Remarks	T, °K (See *Subsection 4.*)	log P_2, torr (Eq. 12)	log P_3, torr (Eq. 13)
0.90	2, 362	213.16	—	2.167	S	213.16	−4.726	2.129
0.90		188.76	—	1.367	F	189.01	−6.594	1.361
0.85		184.16	—	1.155	F	183.71	−6.628	1.103
0.85		213.16	—	2.135	S	213.16	−4.341	2.074
0.812		180.16	—	0.956	Q, F	178.74†	−6.790†	0.847†
0.80		181.96	—	1.022	F	181.35	−6.463	0.931
0.80		223.16	—	2.365	S	223.16	−3.396	2.281
0.75		189.31	—	1.248	F	189.45	−5.442	1.146
0.70		223.16	—	2.245	S	223.16	−2.891	2.113
0.70		193.46	—	1.320	F	193.61	−4.831	1.190
0.6667		194.36	—	1.306	N, F	194.36†	−4.603†	1.137†
0.65		194.16	—	1.240	F	194.19	−4.533	1.088
0.65		223.16	—	2.156	S	223.16	−2.677	2.010
0.60		223.16	—	2.043	S	223.16	−2.482	1.893
0.60		189.31	—	0.934	F	191.36	−4.509	0.841
0.5855		186.81	—	0.813	Q, F	189.91	−4.553	0.740
0.55		191.16	—	0.0820	F	191.77	−4.264	0.699
0.50		193.96	—	0.732	N, F	193.91‡	−3.918‡	0.609‡
0.50		243.16	—	2.278	S	243.16	−1.176	2.166
0.45		193.16	—	0.508	S	193.16	−3.796	0.386
0.45		191.31	—	0.432	F	191.76	−3.894	0.328
0.40		184.16	—	−0.174	F	185.24	−4.203	−0.178
0.35		263.16	—	2.248	S	263.16	−0.038	2.202
0.35		173.26	—	−1.046	S	174.03	−4.930	−0.995
0.346		172.86	—	−1.081	Q, F	172.96‡	−5.007‡	−1.075‡
0.30		273.16	—	2.292	S	273.16	0.392	2.264
0.30		204.46	—	0.204	F	196.20	−3.177	−0.179
0.25		227.16	—	0.806	F	217.36	−1.851	0.419
0.2395	3, 1467	273.16	0.448	2.067	S	273.16	0.476	2.036
0.2181		316.16	1.578	2.760	S	316.16	1.721	2.848
0.2054		273.16	0.477	1.916	S	273.16	0.517	1.892
0.20		241.91	−0.600	1.045	F	234.93	−0.931	0.775
0.1546		273.16	0.613	1.710	S	273.16	0.571	1.646
0.15	2, 362	253.00	—	0.125	F	249.46	−0.268	0.958
0.10	2, 362	261.21	0.215	1.076	F	261.34	0.219	0.988
0.0987	3, 1467	333.16	2.132	2.575	S	333.16	2.212	2.616
0.0964		273.16	0.724	1.394	S	273.16	0.622	1.291
0.05		267.81	0.466	0.868	F	270.87	0.578	0.815
0.0408		333.16	2.159	2.136	S	333.16	2.246	2.136
0.00		—	—	—	S	373.16	3.040	$-\infty$
0.00	2, 363	273.16	0.661	—	F	278.22	0.839	$-\infty$

†Data used to obtain constants in Eq. (10) for $(NH_3)_2H_2O$ hydrate.

‡Data used to obtain constants in Eq. (11) for $(NH_3)H_2O$ hydrate.

Underlined entries indicate data used to obtain constants in Eqs. (12) and (13) for solution region.

S = point of consideration lies in solution region.

F = point of consideration lies on freezing curve.

Q = quadrupole point.

N = nose of freezing curve where the H_2O and NH_3 number ratio are equal in the solution and adjacent hydrate regions.

Table 6. Freezing curve equations

Region of concentration	Quantities eliminated	Source equations	Freezing curves
$0.812 \leq C \leq 1.00$ Solid NH_3	log P_3	(9), (13)	$T = \frac{457.88 + 878.192\,(C^2 - 2C)}{\log C - 0.406 + 1.743\,(C^2 - 2C)}$ (14)
$0.5855 \leq C \leq 0.812$ $(NH_3)_2H_2O$	log P_2 log P_3	(10), (12), (13)	$T = \frac{183.982 - 1170.92C + 878.192C^2}{(1/3)\log [C^2(1 - C)] - 0.01033 - 2.324C + 1.743C^2}$ (15)
$0.346 \leq C \leq 0.5855$ NH_3H_2O	log P_2 log P_3	(11), (12), (13)	$T = \frac{117.29 + 1756.384\,(C^2 - C)}{\log [-(C^2 - C)] - 0.186 + 3.486\,(C^2 - C)}$ (16)
$0.0 \leq C \leq 0.346$ Solid H_2O	log P_2	(8), (12)	$T = \frac{-266.81 + 878.192C^2}{\log (1 - C) - 0.959 + 1.743C^2}$ (17)

$C = 0.25$. The next largest freezing curve discrepancies occur at the quadrupole points: at $C = 0.5855$, T is 3°K below table values and at $C = 0.812$, T is 1.4°K below table value. However, the log P_3 values remain within 0.11 of the tabular values there.

A phase diagram of the NH_3–H_2O system was constructed (Fig. 1) for comparison with the phase diagram from Ref. 1. Lines of constant concentration are straight and range from $0.01 \leq C \leq 0.999$. Isothermal curves range from $T = -100$°C to $T = +40$°C. Equations (12) and (13) were used to plot the solution region. The freezing curves (Eqs. 14 to 17) were used to plot the solid–solution boundaries. The lines separating two solid phases are found by equating two adjacent solid pressure equations and finding the ratio of log P_2 to log P_3.

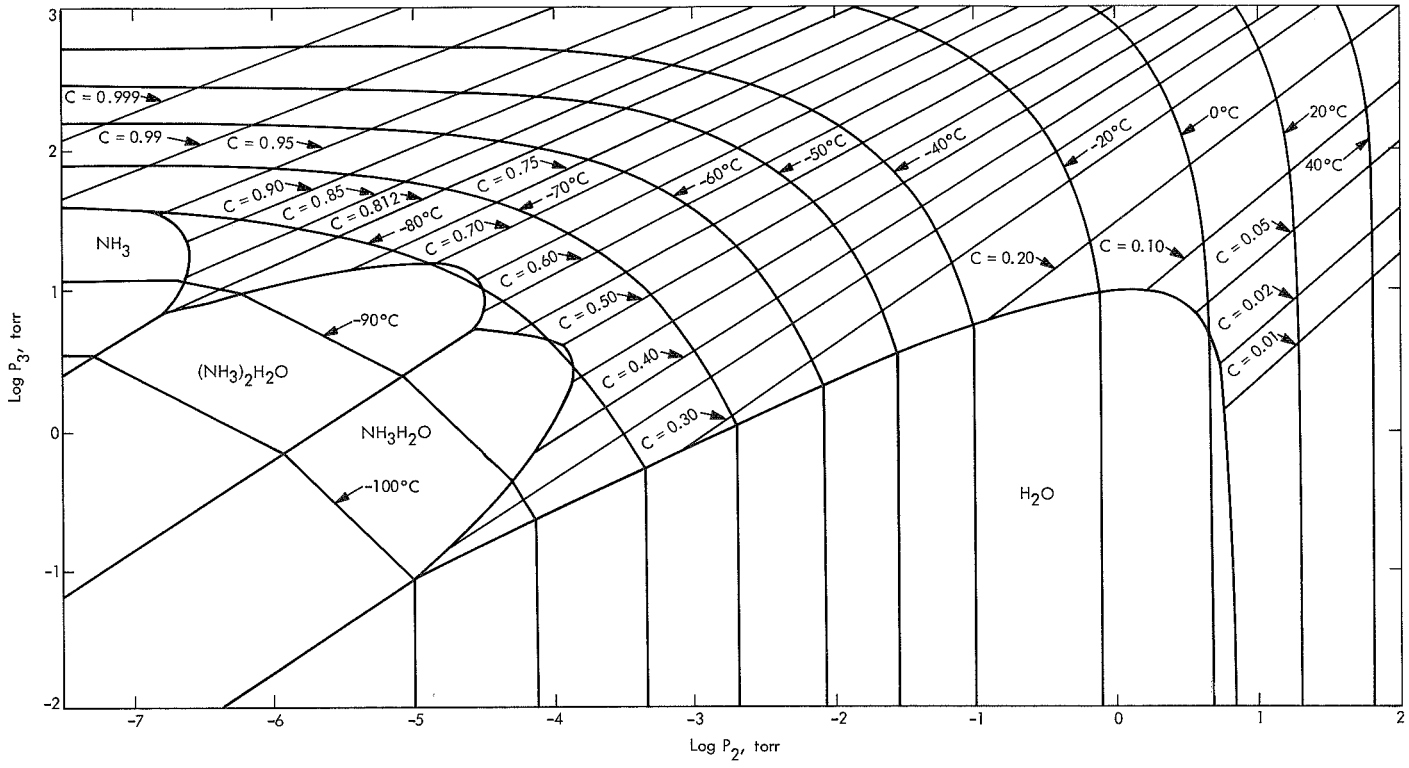

Fig. 1. Phase diagram for the NH_3–H_2O system prepared from Eqs. (8) through (17)

5. Conclusions

Empirical equations produced for all regions agree remarkably well with the table values. Discrepancies over the entire region shown in Fig. 1 are within a factor of about 2.5, with the poorest fit occurring along the freezing curve in the vicinity of $C \simeq 0.25$. Qualitatively the results agree with those of Lewis (Ref. 1), who employed graphical representations of the NH_3–H_2O system rather than analytic ones such as those discussed above. It appears likely that much better fits cannot be obtained without more data and more complicated relations among the quantities of interest.

The relations derived enable one to predict cloud composition and temperature of formation in a model atmosphere containing ammonia and water required for space vehicle design criteria. In particular, the equations were used in preparation of the Jupiter and Saturn environmental design criteria monograph atmospheric models.[1]

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